Correlation of the deactivation of CoMo/Al$_2$O$_3$ in hydrodesulfurization with surface carbon species

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A B S T R A C T

The deactivation of CoMo/Al$_2$O$_3$ in the hydrodesulfurization (HDS) of dibenzothiophene (DBT) was investigated under laboratory conditions that allowed the accelerated deposition of coke on the catalyst. The coke deposition was enhanced at low H$_2$ pressures and when naphthalene was added to the reaction solution. Characterization of deactivated catalysts by elemental analysis (EA) and temperature-programmed oxidation (TPO) identified two types of carbonaceous species deposited on the catalysts, the reactive and the refractory species. The refractory deposit, or hard coke, was a major contributor to the deactivation and, therefore, the amounts of hard coke present on the catalyst determined the overall activity. A correlation was established in this study between the activity and the amounts of deposited hard coke based on the results of accelerated deactivation treatment. A similar relation was also observed between the two parameters when the catalyst was used in an industrial process for long periods. The above findings suggest that the reaction periods of two different scales, i.e., in laboratory and industrial processes, can be correlated with each other based on the amounts of hard coke when coking is the major mechanism of catalyst deactivation.

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1. Introduction

Deep hydrodesulfurization (HDS) of sulfur compounds included in diesel has become an important issue in recent years due to stringent regulations that require low levels of sulfur included in the fuel. Many efforts have been made to meet the requirements, largely by the development of highly active catalysts [1–3]. However, an equally important goal in the efforts should be the development of catalysts of good tolerance to deactivation, i.e., longer lifetimes. Among various factors that are responsible for the deactivation of HDS catalysts, such as promoter segregation [4–11], sintering of MoS$_2$ [5,12–17], poisoning by nitrogen-containing compounds [18–27], deposition of metals [28–33], and coking [32–48], coking is known as a major contributor to the deactivation in many cases concerning industrial processes [1,2,39,41,47,49]. Accordingly, the present study was made about a catalyst that had been deactivated largely by coking in an industrial HDS process.

One of the problems encountered in the study of catalyst deactivation is that the catalysts are relatively robust and therefore require longer periods for deactivation. For example, typical commercial HDS catalysts have a lifetime of 2–4 years in industrial applications [50], which makes it impractical to measure the lifetime in a laboratory. One of the solutions to this problem is to test the catalysts under the conditions of accelerated deactivation such that changes in the catalyst activity can be monitored during relatively short periods. Numerous studies were made about the accelerated deactivation of HDS catalysts, particularly by coke formation [40,51,52]. In these studies, it was important to identify the key factor, or the surface species, that worked as a major contributor to catalyst deactivation, independent of the process conditions. A few studies succeeded in correlating the residual activity of catalysts with the amounts and the specific type of deposited coke [40,52], but there was the other case that failed in establishing the correlation because the properties of deposited coke changed in a complex manner according to the process conditions [51].

In this study, we attempted to find experimental conditions that allowed the accelerated deactivation of the catalyst, particularly by coking. The specific type of coke that was responsible for catalyst deactivation was identified based on the

characterization of deposited coke by elemental analysis (EA) and temperature-programmed oxidation (TPO). We also derived the relationship between two reaction periods of different time scales, i.e., in laboratory and industrial processes, which allowed the same extent of catalyst deactivation by coking. The correlation will be useful for predicting catalyst lifetime in an industrial process based on the time required for catalyst deactivation under laboratory conditions.

2. Experimental

2.1. Accelerated deactivation and activity evaluation

A commercial CoMo/Al$_2$O$_3$ catalyst, which contained Co and Mo in the amounts of 2.5 and 10.1 wt%, respectively, was used for the HDS of dibenzothiophene (DBT, 99% purity) in a 100 ml stirred-batch reactor. Prior to use in the reaction, the catalyst was sulfided in a solution containing 2 wt% of dimethyldisulfide (DMDS) at 623 K for 18 h. Two different schemes of reaction conditions were used depending on the purposes of the tests: the accelerated deactivation of the catalyst and the evaluation of the catalyst activity.

The catalyst was deactivated at accelerated rates by reaction under severe conditions (Condition I) using a mixture containing 0.2 g of the catalyst, 1.5 g of DBT, 30 ml of n-pentadecane as a solvent, and different amounts of naphthalene. Naphthalene was added to the mixture to promote coke deposition on the catalyst. Prior to starting the reaction, an autoclave reactor containing the mixture was purged with nitrogen, its temperature was raised to 653 K at a rate of 5 K/min and finally to 673 K at a rate of 2 K/min. Hydrogen was added to the reactor at different pressures to initiate the HDS reaction. Catalysts recovered from the deactivation treatment, designated as CoMo(x h) where x denotes the deactivation period, were washed with n-hexane in a Soxhlet unit [53] before their residual activities were measured by the activity test.

The activity of the deactivated catalyst was measured under a mild condition (Condition II) using a mixture containing 0.1 g of the catalyst, 0.06 g of DBT, and 30 ml of n-pentadecane. The reaction was carried out at 593 K and at an H$_2$ pressure of 4.0 MPa for 2 h. The product concentrations were analyzed with a gas chromatograph (GC) using a capillary column (HP1; 30 m × 0.53 mm) equipped with a flame ionization detector (FID). Table 1 summarizes the conditions of the above two schemes.

The activities of two CoMo/Al$_2$O$_3$ catalysts, obtained after use in the HDS of diesel for 2 and 4 years in industry, were also evaluated under the above condition (Condition II) for comparison. In industry, the HDS of diesel, containing 1.2 wt% of sulfur, was carried out in a fixed-bed reactor with a processing capacity of 40,000 barrels/day. Two- and four-year operations were conducted at total pressures of 3.2 and 3.9 MPa and at temperatures in the range of from 628 (start of run) to 661 K (end of run) and from 626
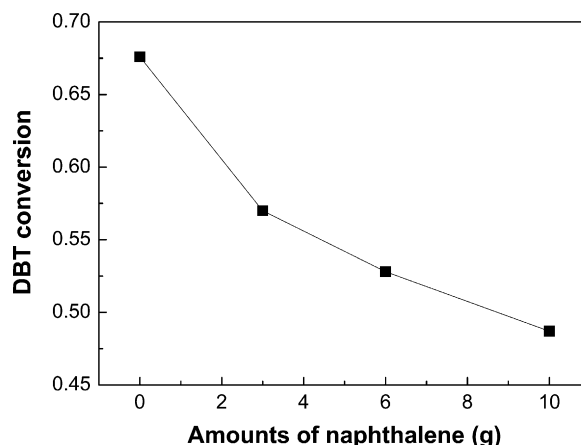

Fig. 1. The effect of naphthalene contained in a reactant solution on the activity of CoMo catalysts for DBT conversion.

to 658 K, respectively. These catalysts were designated as CoMo(2 year) and CoMo(4 year) depending on the operation periods.

2.2. Characterization

The amounts of coke deposited on the catalyst in the deactivation treatment were measured by EA (CE Instrument), and the properties of coke were characterized by TPO. In TPO, the sample was heated from room temperature to 1200 K at a rate of 10 K/min in O$_2$ flowing at 30 sccm, while product gases were analyzed with a mass spectrometer (VG mass, Sensor Lab).

3. Results

3.1. Accelerated deactivation of catalyst

Fig. 1 shows that the catalyst activity, represented by the DBT conversion obtained in the activity test (Condition II), decreased with an increase in the amounts of naphthalene that had been added to the reaction solution in the deactivation treatment (Condition I). Based on the above result, the next series of deactivation treatments were made at different H$_2$ pressures while the amount of added naphthalene was fixed at 10 g. The residual activity obtained after the treatment decreased nearly in parallel with the H$_2$ pressure, as shown in Fig. 2. Consequently, it was decided that the accelerated deactivation treatment should be at an H$_2$ pressure of 1.0 MPa using a reactant solution that contained
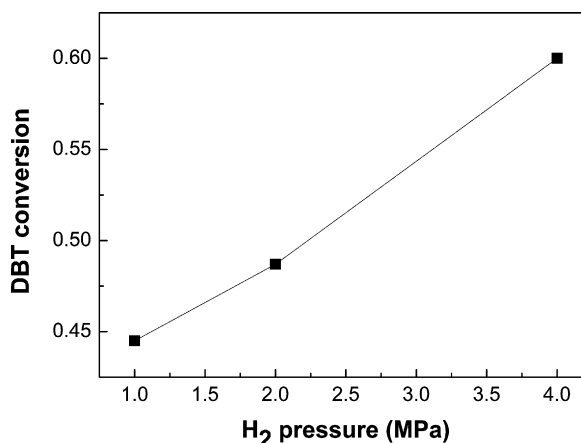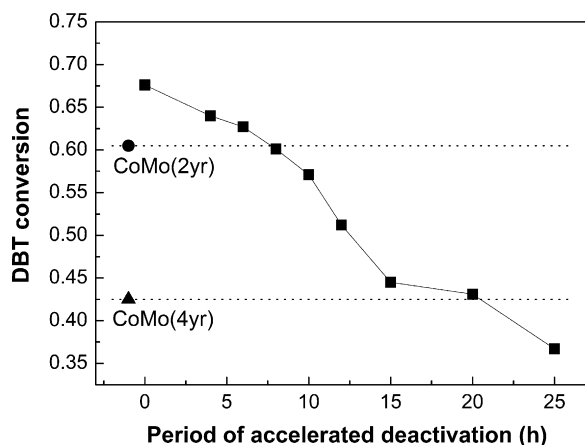
Table 1
Conditions of the accelerated deactivation treatment and the activity test

	Accelerated deactivation (Condition I)	Activity test (Condition II)
Catalyst (g)	0.2	0.1
Dibenzothiophene (g)	1.5	0.06
n-Pentadecane (ml)	30	30
Temperature (K)	673	593
H$_2$ pressure (MPa)	1.0–4.0	4.0
Reaction period (h)	2–25	2
Naphthalene (g)	3–12	–

Fig. 2. The effect of H$_2$ pressure on the activity of CoMo catalysts for DBT conversion.

Fig. 3. The effect of the deactivation reaction period on the activity of CoMo catalysts for DBT conversion.

10 g of added naphthalene. Fig. 3 shows changes in the activity of the catalyst after use for DBT HDS under the deactivation condition (Condition I) for different periods. Although the data are somewhat scattered, it is apparent that the activity was lowered nearly in proportion to the period of the treatment. In Fig. 3, it is noteworthy that catalysts that had been deactivated in a laboratory process for 8 and 20 h showed nearly the same conversions as those used in an industrial process for 2 and 4 years, respectively.

3.2. Characterization of deactivated catalysts

3.2.1. Elemental analysis (EA)

Table 2 shows the amounts of C and H elements contained in sample catalysts of this study. The C content increased with the reaction period independent of whether the catalyst was deactivated in an industrial or in a laboratory process. On the other hand, the H content changed in different manners according to the processes. That is, the amounts of hydrogen increased after use in an industrial process but decreased after accelerated deactivation in a laboratory process. The H contents of laboratory-used catalysts were nearly the same, 1.14–1.24 wt%, regardless of the deactivation periods. The H/C atomic ratio decreased with the extents of catalyst deactivation for all cases and became lower than 1.0 for CoMo(25 h).

The above results suggest that the deposition of the carbon species was the major cause of catalyst deactivation in both processes and that the surface species gradually became H-

Table 2
The amounts of individual elements contained in the sample catalysts of this study

Catalysts	Amounts of elements (wt%)		H/C atomic ratio
	C	H	
CoMo(fresh), after sulfidation	2.68	1.58	7.02
After use in an industrial process			
CoMo(2 year)	7.60	1.67	2.62
CoMo(4 year)	24.90	3.81	1.82
Accelerated deactivation in a laboratory process			
CoMo(4 h)	5.19	1.14	2.62
CoMo(8 h)	5.88	1.24	2.51
CoMo(10 h)	6.13	1.23	2.38
CoMo(15 h)	8.23	1.18	1.70
CoMo(20 h)	10.36	1.19	1.22
CoMo(25 h)	13.83	1.14	0.99

deficient with an increase in the extents of deactivation. The other point is that the carbon species deposited on the catalyst in an industrial process were richer in hydrogen than those deposited in an accelerated deactivation process. It was shown in Fig. 3 that CoMo(8 h) and CoMo(20 h) were deactivated to the same extent as CoMo(2 year) and CoMo(4 year), respectively. However, these results are not in accordance with those in Table 2. That is, CoMo(8 h) and CoMo(2 year) had somewhat similar carbon contents and H/C ratios, but CoMo(20 h) had significantly lower carbon content and H/C ratio than in the case of CoMo(4 year). This discrepancy in the amounts of carbon species between the latter two catalysts, in spite of their same extent of deactivation, suggests that the carbon content and the H/C ratio are not proper parameters to be correlated with the extents of catalyst deactivation. Consequently, we further investigated the properties of carbon species deposited on the catalysts, as described below.
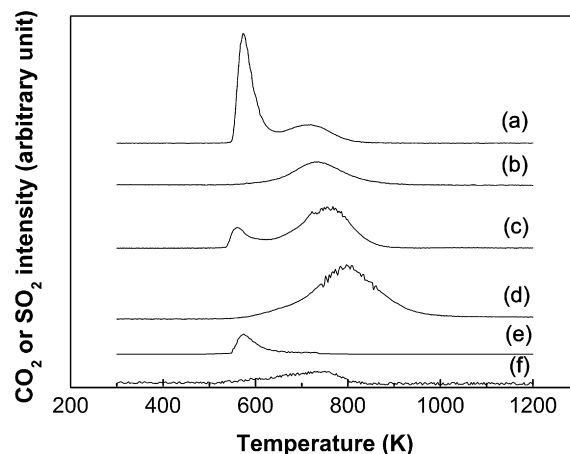
3.2.2. Temperature-programmed oxidation (TPO)

In Fig. 4, the TPO of CoMo(4 year), case (a), shows two characteristic peaks of CO_2, one with a high intensity centered at about 600 K and the other with a lower intensity at 700 K, while the TPO of CoMo(20 h), case (b), shows only one at 700 K. Accordingly, it can be concluded that CoMo(4 year) contains two types of carbon species, according to their reactivity with oxygen, while CoMo(20 h) contains only one that is oxidized at relatively high temperatures. The two carbon species were defined in previous studies [54,55] as the reactive (soft) coke, which could be removed easily during HDS at 600 K, and the refractory (hard) coke, which was difficult to remove from the catalyst surface. The results in Fig. 4 are in accordance with those in Table 2, which shows a higher H/C ratio for CoMo(4 year) than for CoMo(20 h), considering that the reactive coke is richer in hydrogen than the refractory one [37,56]. It is noteworthy in Fig. 4 that the intensities of the peaks corresponding to the refractory coke were nearly the same for two catalysts, CoMo(4 year) and CoMo(20 h), which strongly suggests that the extent of catalyst deactivation was determined largely by the amounts of the refractory coke instead of the total amounts of carbon species deposited on the catalysts. The TPO results obtained with CoMo(2 year), case (c), and CoMo(8 h), case (d), show the same trend as the above, although in this case the intensity of the reactive coke, observed with CoMo(2 year), was lower than that of the refractory coke.

The surface species of CoMo(4 year) were further analyzed by measuring the amounts of SO_2 produced in the TPO. As shown in

Fig. 4. CO_2 or SO_2 peaks observed in the TPO of (a) CoMo(4 year), (b) CoMo(20 h), (c) CoMo(2 year), (d) CoMo(8 h), (e) CoMo(4 year) (SO_2 signal), and (f) treated-CoMo(4 year).

case (e), an intense SO_2 peak was observed nearly at the same temperatures as for the CO_2 peak originating from the reactive coke. The results indicate that the reactive coke contained both sulfur and carbon whereas the refractory coke contained only carbon. Fig. 4 also shows the TPO result obtained with treated-CoMo(4 year), case (f), which had been treated in a reaction solution and under the conditions that were identical to those used for the reaction test. Contrary to the case of untreated-CoMo(4 year), case (a), which shows two peaks at 600 and 700 K, the treated one shows only one peak at 700 K. This result indicates that the reactive coke was nearly completely removed from the catalyst by the above treatment while the refractory one was retained on it. It is likely that the reactive coke was removed either by dissolution in the solution or by reaction with hydrogen in the treatment step. Regardless of the mechanism involved in the coke removal, it is apparent that the reactive coke is "more reactive" than the refractory one.

4. Discussions

4.1. Origin of catalyst deactivation

Although it was suggested in the above that coking was the major cause of catalyst deactivation in this study, it can be justified by more rigorous discussions given below.

Firstly, catalysts are deactivated by metal deposition when the feed contains the metal compounds as impurities. The spent catalysts of this study, obtained from an industrial process to treat diesel (gas oil), contained no impurity metals as confirmed by inductively coupled plasma (ICP). The solution used in the laboratorial tests for the accelerated deactivation of catalysts contained only DBT and naphthalene. Accordingly, metal deposition can be excluded from possible reasons for the deactivation.

Secondly, the MoS_2 crystallites can sinter when the catalysts are exposed to high temperatures during either sulfidation or hydrotreating process. The fresh catalyst of this study, used for either industrial or laboratorial process, was obtained by sulfidation under the identical condition, at 623 K for 18 h. Accordingly, the observed different extents of catalyst deactivation were obtained in the subsequent HDS process. The possibility of catalyst sintering during the HDS process of this study, carried out either at 626–661 K for 2–4 years or at 673 K for up to 25 h, is discussed below.

Pedraza et al. observed the significant sintering of unsupported MoS_2 catalysts [13] but no sintering of NiMoS catalysts [15], which were used for thiophene HDS at 623–653 K. They explained that the difference in the sintering of two catalysts was observed because Ni atoms localized at the edge sites of MoS_2 slabs stabilized the latter, leading to the suppression of sintering. A recent study about the aging of $CoMoP/Al_2O_3$ and $NiMoP/Al_2O_3$ during the HDS of diesel at 593–650 K for 1–2 years [11] reported that there was no effective change in the MoS_2 crystallite morphology, both in slab size and stacking, before and after HDS. This result agrees with one reported by Eijsbouts et al. [10] who observed no major changes in the MoS_2 morphology of commercial Type 2 $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ in the HDS of various oils at 593–653 K for 5–8 days.

Considering that the temperature ranges of the above studies were similar to one used in the present study, it can be concluded that sintering was not the major factor to be responsible for the catalyst deactivation observed in this study.

Thirdly, the segregation of promoter was previously indicated as one of reasons for the catalyst deactivation [4–11]. For instance, Breysse et al. [7] observed Co segregation in unsupported CoMoS catalysts in the HDS of DBT carried out at 493–673 K; Koranyi et al.

[8] studied Co segregation in unsupported and Al_2O_3-supported CoMoS catalysts in the HDS of thiophene at 673 K to observe that the segregation proceeded to greater extents with the former catalyst than with the latter; Günter et al. [9] showed the segregation of Co_9S_8 during the sulfidation of unsupported CoMo oxide catalysts at 673 K. According to a review about the flexibility of the active phase of HDS catalysts [4], MoS_2 crystallites can migrate over Al_2O_3 surface and sinter during hydroprocessing, leading to the consecutive Co or Ni segregation because the number of edge sites at which promoters can be located gradually decreases due to MoS_2 sintering. Eijsbouts et al. [10] studied the properties of Type 2 $CoMoS/Al_2O_3$ and $NiMoS/Al_2O_3$ catalysts, which were used in the HDS of various feeds at 613–683 K and at 30–100 bar of H_2 pressure. Whereas $NiMoS/Al_2O_3$ exhibited a significant segregation of Ni sulfide, Co segregation was not observed. They suggested that Co_9S_8 aggregated less rapidly than Ni_3S_2 owing to its higher Tamman temperature.

Accordingly, catalyst deactivation by promoter segregation was not likely to occur in this study as there was no significant sintering of MoS_2 crystallites and, additionally, the catalysts of this study were promoted by Co instead of Ni.

However, one of the latest studies about the deactivation of HDS catalysts [11] showed that the segregation of Ni and Co was the main reason for catalyst deactivation in the HDS of diesel. Their HDS conditions were similar to those used in our study.

Concerning the above study, it should be pointed out that the origin of promoter segregation was related to the coke species deposited on the catalyst. The hydrogenation activities of fresh and spent CoMoS catalysts were linearly related to the amounts of Co in mixed CoMoS phase, as quantified by XPS analysis. However, a significant part of Co was not quantified by XPS and it was considered that the loss of Co signal was due to the segregation of Co atom in the carrier or inside the coke that could mask the Co signal. Moreover, it was suggested that coke precursors adsorbed at the MoS_2 edge sites might affect the segregation of Co and Ni.

All these explanations reveal that both coke formation and promoter segregation are related with each other and do not occur independently. Therefore, we suggest in our study that the activity of $CoMo/Al_2O_3$ catalysts which were deactivated in different periods can be correlated with the amounts of coke although Co segregation may take place.

Finally, the diffusion of reactants and products may be inhibited due to the blockage of pores by deposited coke, which is significant when coke is distributed non-uniformly in the catalyst pellet. However, the observed reaction rates were not affected by the diffusion limitation when the catalyst size was very small (75–125 μm) [5]. As the catalyst powders of this study were in the range of ca. 150 μm, the possibility of rate modification due to diffusion limitation can be excluded.

4.2. Mechanism of coke formation

Fig. 5 shows changes in the C contents of the catalyst with the periods of the laboratory deactivation process, which is obtained from the data given in Table 2. The C contents largely represent the amounts of the refractory coke, which are the major species produced during the laboratory deactivation process. Fig. 5 also shows the C contents of CoMo(2 year) and CoMo(4 year) at the process periods corresponding to those of CoMo(8 h) and CoMo(20 h), which exhibited similar HDS activities as the former catalysts. The C contents of the industry-used catalysts became similar to those of the laboratory-used ones when the C contents of the former catalysts were re-calculated such that they represented only the refractory coke species, as identified by a TPO peak at 700 K.
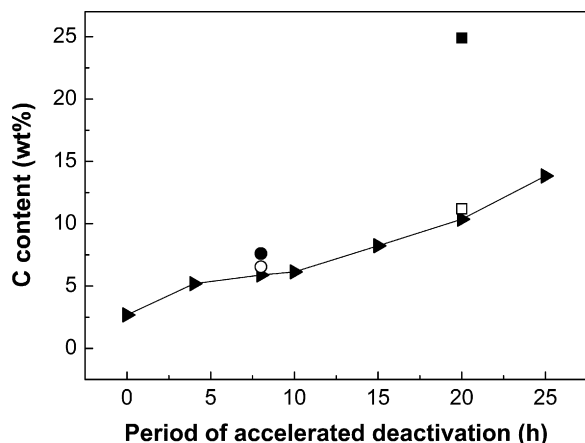
Fig. 5. C contents of CoMo catalysts deactivated in a laboratory process (▶), CoMo(2 year) (●: total, ○: refractory coke) and CoMo(4 year) (■: total, □: refractory coke).

It is somewhat unexpected that the C content of the fresh catalyst was non-zero, although fresh catalyst was supposed to be exempt from the coke deposition. One of the possible sources of the C species in the fresh catalyst is the residue of DMDS that was incompletely decomposed in the catalyst sulfidation step. This is likely because temperature used in this study for the sulfidation, 623 K, was not high enough to guarantee the complete decomposition of DMDS [57,58].

The amounts of coke increased continuously with the periods of the deactivation process, although the rates of coke formation were higher during the initial period, less than 4 h, than during the later periods, which is consistent with the results of previous studies [38,59]. According to the mechanism of coke formation, aromatic compounds are produced by the cyclic condensation of relatively reactive aliphatic compounds that have been formed on the catalyst, and eventually polymerized to asphaltenes to become precursors of the refractory (hard) coke [56]. Consequently, the structure of the refractory coke is believed to be highly polyaromatic.

4.3. Catalyst deactivation by the refractory coke

In Fig. 6, the activities of deactivated catalysts, indicated by the DBT conversions, were plotted against the C contents of the catalysts that represented the amounts of the refractory coke. The results of Fig. 6 look similar to those of Fig. 3, which is a plot of the conversions against the periods of the deactivation process, but
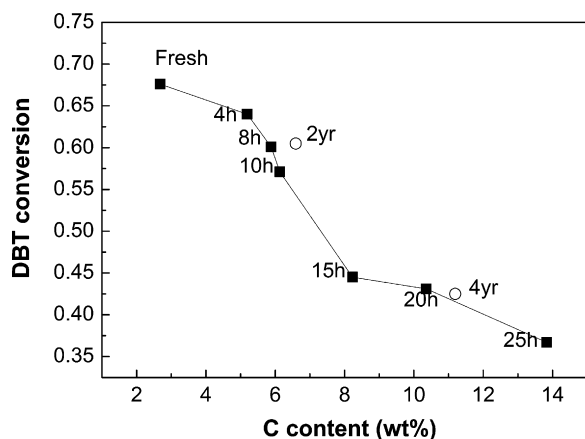

Fig. 6. DBT conversions of various CoMo catalysts as a function of the C contents representing the amounts of the refractory coke.

Fig. 6 is based on a factor that is directly responsible for the catalyst deactivation. The significance of Fig. 6 is that the catalyst activities were successfully correlated to a single parameter, the amounts of the refractory coke, although the time scales of the two deactivation processes were extremely different.

Fig. 6 shows that the rates of catalyst deactivation, represented by the slope of the curve, were relatively low at the initial stage when the C contents were lower than 5 wt% and became higher at the middle stage when the C contents were between 5 and 8 wt%. The rates finally decreased again at the later stage when the C contents were higher than 8 wt%. The slow deactivation of the catalyst at the initial stage, which is in accordance with previous reports [37,54], was observed because the coke species formed at this stage were rich in H, as shown in Table 2, and therefore were relatively reactive. The deactivation rates increased at the middle stage when the active sites of the catalyst were covered with the H-deficient, refractory coke species. At the later stage, when relatively large amounts of coke had accumulated on the catalyst, the coke species were expected to stack, either on themselves or on the catalytically inactive sites of dispersed MoS_2 slabs, and consequently the rates of catalyst deactivation decreased again, as observed in Fig. 6.

The above results that show a correlation between the amounts of the refractory coke and the extents of catalyst deactivation can be discussed in comparison with those of previous studies in which similar investigations were made. Tanaka et al. [51] reported that the residual activity of deactivated CoMo catalysts, either in accelerated or normal process, was determined by the amounts of deposited coke with high aromaticity. However, they failed in correlating the catalyst activity with the specific type of coke because the amounts and the aromaticity of coke varied depending on the deactivation processes. On the other hand, Trejo and Albertos [52] observed a correlation between the activity and the amounts of deposited coke for $NiMo/Al_2O_3$ catalyst, which was used either in an accelerated deactivation test or in an industrial process. But coke deposited on the catalyst had different reactivity toward oxygen depending on the deactivation processes, as indicated by different shapes and positions of peaks observed in the TPO of deposited coke. Ammus et al. [37] reported that the activity of CoMo catalysts in a commercial HDS unit decreased rapidly at the later stage of the process when the C/H ratio of deposited coke increased and consequently the reactivity of the coke decreased. Song and Ihm [40], who deposited the coke species of different aromaticity on $CoMo/Al_2O_3$ using various coke precursors, proposed that the lifetime of the catalyst in an industrial process could be correlated with the aromaticity of deposited coke. Seki and Yoshimoto [60] also correlated the deactivation of NiCoMo catalyst with the aromaticity of asphaltenes, which were present as reactants in the HDS process and became precursors of "hard coke" deposited on the catalyst. The results of the above two studies [40,60] are in accordance with one reported by Ammus et al. [37] and also with that of present study, considering that the coke species with high aromaticity have high C/H ratios and low reactivity so as to be called as the refractory coke.

5. Conclusions

Based on the above experimental results and discussions, the following conclusions can be made about the mechanistic and parametric aspects of catalyst deactivation by coking in the HDS process. Between the two types of coke species that were formed on the catalyst in the HDS process, the refractory coke, which was highly aromatic and had relatively low reactivity toward oxygen, was found to be a major contributor to catalyst deactivation. The

amount of the refractory coke could be used as a single parameter to determine the periods of different HDS processes, which may have extremely different time scales as in the cases of laboratory and industrial processes, that allow the same extent of catalyst deactivation. Conditions in the laboratory process that enhanced the deposition of the refractory coke species on the catalyst were identified in this study, and these could be used for the accelerated deactivation of HDS catalysts by coking.

Acknowledgements

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